

THE DEGREE OF CRYSTALLINITY OF MULTICOMPONENT POLYMERS BY WAXD*

MO Zhishen(莫志深) YANG Baoquan(杨宝泉) and ZHANG Hongfang(张宏放)

(Polymer Physics Laboratory, Changchun Institute of Applied Chemistry,
Academia Sinica, Changchun 130022)

ABSTRACT

Based on the X-ray scattering intensity theory, the correction factors of the degree of crystallinity formulae of the multicomponent polymers have been clearly defined. The formulae of the degree of crystallinity of the multicomponent polymers were derived in terms of WAXD theory and improved graphic multipeak resolution methods. The results calculated are satisfactory in comparison with the density measurement.

INTRODUCTION

The degree of crystallinity ($W_{c,x}$) is one of the important parameters for a crystalline polymer. The physical and mechanical properties of polymers are profoundly dependent on the degree of crystallinity. Although X-ray diffraction analysis has been widely used to determine $W_{c,x}$ of homopolymers^[1,7,9], the $W_{c,x}$ for the multicomponent polymers have not been correctly determined so far. In the present paper, the formulae of the multicomponent polymers $W_{c,x}$ were derived in terms of the X-ray diffraction intensity theory and improved graphic multipeak resolution methods.

EXPERIMENTAL

1. Block copolymer synthesis

Ethylen (E) - Propylene (P) block copolymers were synthesized by sequential slurry polymerization with δ -TiCl₃-Et₂AlCl in hexane^[2,3]. Homopolymers of isotactic polypropylene (*i*-PP) and polyethylene (PE) and ethylene-propylene copolymers (EPR) were prepared with the same catalyst.

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2. Mechanical blends

i-PP and EPR granules with compositions as the same as those of the block copolymers were mixed cold and compression—molded into sheets, which were repeatedly cut into pieces and remolded at least five times.

3. WAXD specimens

Polymer samples were heat—molded into sheets, which were cut into pieces, put into a $20 \times 15 \times 1.5$ mm mold, and heated above melting point ca. 20°C under a pressure of $9.81 \times 10^6 \text{ N/m}^2$ for 5 min. The samples were then transferred to another press of less than ca. 20°C of melting point and $9.8 \times 10^6 \text{ N/m}^2$ and let stand to cool to ambient temperature. If the sample is anisotropic, a suitable average of the diffracted intensity in reciprocal space can be obtained.

4. WAXD measurement

WAXD patterns were taken on a Rigaku D/max-IIB diffractometer: $\text{CuK}\alpha_1$ radiation with a graphite crystal monochromator, voltage 35 kV, current 15 mA, divergence slit 1° , receiving slit 0.3 mm, and scattering slit 1° . The angular scale and recorder reading (2θ) were calibrated to an accuracy of $\pm 0.01^\circ$. Scans in reflection mode were performed through the 2θ range $5\text{--}40^\circ$.

5. Calculation of the degree of crystallinity for homopolymer

The degree of crystallinity determined by X-ray diffraction is calculated by graphic multippeak resolution method previously established^[1,4,6] as follows:

$$W_{c,x} = \frac{\sum_i C_{i,hkl}(\theta) I_{i,hkl}(\theta)}{\sum_i C_{i,hkl}(\theta) I_{i,hkl}(\theta) + k_i C_a(\theta) I_a(\theta)} \times 100\% \quad (1)$$

where $I_{i,hkl}$ = relative intensity of the crystalline peaks, $I_a(\theta)$ = relative intensity of the amorphous peak; $C_{i,hkl}(\theta)$ = correction factor of crystalline peaks; $C_a(\theta)$ = correction factor of amorphous peak; the calibration constant $Kx = C_a(\theta) \cdot k_i$, $k_i = \Sigma I_{i,\text{cal}} / \Sigma I_{i,\text{total}}$ ($k_i \leq 1$); k_i is the relative scattering coefficient, which is the ratio of calculated diffraction intensity ($\Sigma I_{i,\text{cal}}$) to total scattering intensity ($\Sigma I_{i,\text{total}}$) for the crystalline polymer specimen of unit weight. $C_{i,hkl}(\theta)$ or $C_a(\theta)$ can be calculated by the following equation:

$$\begin{aligned} C_{i,hkl}^{-1}(\theta) \text{ or } C_a^{-1}(\theta) &= \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} f_i^2 \cdot e^{-2B(\sin 2\theta / \lambda)^2} \\ &= \sum_i N_i f_i^2 \frac{1 + \cos^2 2\theta}{\cos \theta \sin^2 \theta} e^{-2B(\sin 2\theta / \lambda)^2} \end{aligned} \quad (2)$$

where f =atomic scattering factor of a repeating unit, f_i =scattering factors of the i th atom, N_i =number of the its atom in a repeating unit, 2θ =Bragg angle, $(1+\cos^2 2\theta)/\sin^2 \theta \cos \theta$ =angle factor (LP), $e^{-2B(\sin \theta / \lambda)^2}$ =temperature factor(T), and $2B=10$.

The atomic scattering factor f_i can be expressed approximately by:

$$f_i(\sin \theta / \lambda) = \sum_{i=1}^4 a_i e^{-b_i (\sin \theta / \lambda)^2} + C \quad (3)$$

where values of a_i , b_i and c are given in Ref[8].

6. Calculation of the degree of crystallinity for multicomponent polymer

Although X-ray diffraction analysis has been widely used to determine $W_{c,x}$ for homopolymers, those for the multicomponent polymers have not been correctly determined so far. Recently in our paper, the formulae of the multicomponent polymers $W_{c,x}$ was derived in terms of the X-ray scattering intensity theory and improved graphic multipeak resolution method^[1,5,6]. The $W_{c,x}$ of the multicomponent polymers is defined as

$$W_{c,x} = \frac{\sum_{t=1}^M \sum_{j=1}^{P(M)} C_{t,j}(\theta) I_{t,j}(\theta)}{\sum_{t=1}^M \sum_{j=1}^{P(M)} C_{t,j}(\theta) I_{t,j}(\theta) + \sum_{t=1}^M \sum_{l=1}^{N(M)} K_t C_{t,l}(\theta) I_{t,l}(\theta)} \times 100\% \quad (4)$$

where M is the number of the components in the multicomponent polymers, P is the number of Bragg peaks, N is the number of amorphous peaks. $C_{t,j}(\theta)$ is the correction factor of type j Bragg peak and the $C_{t,l}(\theta)$ is the correction factor of type l amorphous peak in the t th component. $I_{t,j}(\theta)$ is the Bragg peak intensity of type j and $I_{t,l}(\theta)$ is the amorphous peak intensity of type l in the t th component, $K_t = \Sigma I_{t,cal} / \Sigma I_{t,total}$ ($K_t \leq 1$). The $C(\theta)$ value can be calculated by Equation (2).

RESULTS AND DISCUSSION

Using Eq. (4), the degree of crystallinity of some typical multicomponent polymers were calculated. Fig. 1 and 2 were WAXD curves of ethylene (E)-propylene (P) copolymer and ethylene (E)-propylene (P) blend, respectively. One of the common features of WAXD patterns of copolymer (Fig. 1) and blend (Fig. 2) is the retention of the modification of the monoclinic i -PP crystalline structure. Also diffractions of the PE crystal planes 110 and 200 are observed in Fig. 1 and 2. The calculation of degree of

crystallinity must consider the contribution from *i*-PP, γ peak and PE, respectively. The amorphous peaks of *i*-PP and PE are at $2\theta = 16.3^\circ$, and 19.5° , respectively. The $W_{c,x}$ was calculated from the data of Table. 1 and 2. by the following equations

$$W_{c,x} = \frac{\Delta_1 + \Delta_2}{\Delta_1 + \Delta_2 + \Delta_3} \times 100\% \quad (\text{for copolymer}) \quad (5)$$

where, $\Delta_1 = (I_{110} + 1.64I_{040} + 2.16I_{130} + 2.73I_\gamma + 2.91I_{111})_{PP}$

$$\Delta_2 = (5.37I_{110} + 6.86I_{200})_{PE} \quad \Delta_3 = 3.4I_{aPE} + 1.29I_{aPP}$$

$$W_{c,x} = \frac{\square_1 + \square_2}{\square_1 + \square_2 + \square_3} \times 100\% \quad (\text{for blend}) \quad (6)$$

where, $\square_1 = (I_{110} + 1.60I_{040} + 2.16I_{130} + 2.68I_\gamma + 3.18I_{111})_{PP}$

$$\square_2 = (5.29I_{110} + 6.88I_{200})_{PE} \quad \square_3 = 3.3I_{aPE} + 1.27I_{aPP}$$

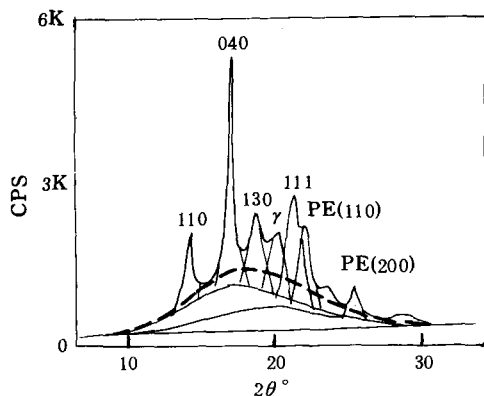


Fig. 1 Resolution of WAXD curve of ethylene-propylene copolymer

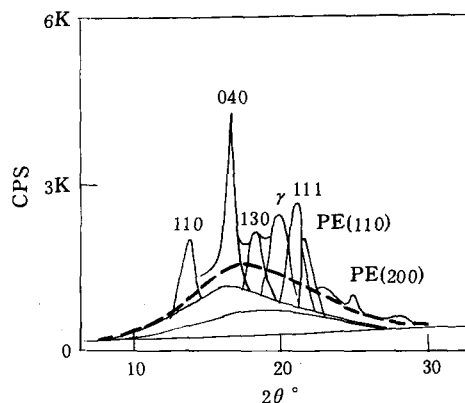


Fig. 2 Resolution of WAXD curve of ethylene-propylene blend

Table 1 The calibration factor of $W_{c,x}$ in E-P copolymer*

Polymers	<i>hkl</i>	$2\theta^\circ$	θ°	<i>T</i>	<i>L_p</i>	<i>f</i> ²	<i>C</i> (θ)	<i>I</i>
PE	110	21.76	10.88	0.861	53.24	47.39	5.37	5.51
	200	23.45	11.73	0.841	45.55	44.38	6.86	3.52
	A	19.5	9.75	0.886	66.82	51.54	3.82	35.64
PP	110	13.89	6.95	0.940	133.84	92.69	1	6.70
	040	16.74	8.37	0.915	91.45	84.99	1.64	20.02
	130	18.44	9.22	0.898	74.98	80.26	2.16	6.05
	γ	19.95	9.98	0.881	63.74	76.06	2.73	16.92
	111	21.10	10.55	0.969	56.76	72.89	2.91	28.90
	A	16.30	8.15	0.919	96.57	86.20	1.52	81.40

Table 2 The calibration factor of $W_{c,x}$ in E-P blend*

Polymers	hkl	$2\theta^\circ$	θ°	T	L_p	f^2	$C(\theta)$	I
PE	110	21.84	10.92	0.860	52.83	47.25	5.29	20.1
	200	23.64	11.82	0.838	44.79	44.04	6.88	7.6
	A	19.50	9.75	0.886	66.82	51.54	3.72	90.7
PP	110	14.04	7.02	0.939	130.94	92.30	1	5.5
	040	16.76	8.38	0.916	91.23	84.93	1.60	28.4
	130	18.60	9.30	0.896	73.66	79.82	2.16	9.7
	γ	20.00	10.00	0.881	63.41	75.93	2.68	13.9
	111	21.14	10.57	0.868	56.53	72.78	3.18	33.7
	A	16.30	8.15	0.919	96.57	86.20	1.49	66.5

* A is the amorphous peak; $C_{110}(\theta)$ is the standard of normalization for $C_{hkl}(\theta)$; γ peak is a contribution of long E and P sequences in EPR; $k_i(\text{PE})=0.89$; $k_i(\text{PP})=0.85$

The PP/(ethylene-propylene-octene-1)(EPO) copolymer and poly(ethylene oxide) (PEO)/(poly(hydroxy ether) of bisphenol A) (PBHE) blends results are given in Table. 3 and 4. The results above calculated are compatible with the density measurement^[5].

Table 3 $W_{c,x}$ of PP/EPO blends^[5]

PP/EPO(weight)	100/0	90/10	80/20	70/30	50/50	30/70	10/90	0/100
$W_{c,x}\%$	57.2	56.5	51.3	45.4	32.9	24.5	6.9	3.8

Table 4 $W_{c,x}$ of PEO/PBHE blends^[10]

PEO/PBHE(weight)	100/0	90/10	70/30	50/50	40/60	30/70	20/80
$W_{c,x}\%$	90.3	89.6	78.9	69.6	54.7	46.1	0

Keywords:

Multicomponent crystalline polymers; Degree of crystallinity; WAXD

REFERENCES

- [1] Mo, Z. S and Zhang, H. F. , *Polymeric Materials Science and Engineering (in Chinese)*, **1988**, 3, 9; Mo, Z. S. ; Yang, B. Q. and Zhang, H. F. , *Chinese Chemical Letters (CCL)*, **1991**, 2(4), 231.
- [2] Wang, L. X. ; Hu, B. Y. and Huang, B. T. , *Polym. Comm. (in Chinese)*, **1984** (5), 305.
- [3] Mo, Z. S. ; Wang, L. X. ; Zhang, H. F. , et al, *J. Polym. Sci. , Part B; Polym. Physics*, **1987**, 25, 1829.
- [4] Hsieh, You-Lo. and Mo, Z. S. , *J. Appl. Polym. Sci.*, **1987**, 33, 1479.

- [5] Gao, H. ; Mo, Z. S. ; Zhang, H. F. , et al. , *Chinese J. Appl. Chem.*, **1990**, 7(2), 35.
- [6] Mo, Z. S. , *Polymer Bulletin (in Chinese)*, **1992**, 1, 26.
- [7] Ruland, W. , *Polymer*, **1964** a, 5, 89;
Ruland, W. , *Acta Cryst.* , **1961**, 14, 1180.
- [8] International Tables for X-ray Crystallography, Kynoch, 1974, Vol. 4, p. 71, 101.
- [9] Mo, Z. S. ; Lee, K. -B. ; Moon, Y. B. , et al, *Macromolecules*, **1985**, 18, 1972.
- [10] Mo, Z. S. ; Xue, X. F. ; Guo, Q. P. , et al. , *Acta Polymerica Sinica (in Chinese)*, **1991**, (1), 1.